Preparation and Characterization of $YBa_2Cu_3O_{7-\delta}$/Polypyrrole Bilayer Structures

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Abstract: Electrochemical techniques are exploited to fabricate conductive polymer/high-T_c superconductor bilayer structures. Scanning electron microscopy, atomic force microscopy, and electrochemical techniques are utilized to characterize the electrodeposition of polypyrrole layers grown onto $YBa_2Cu_3O_{7-\delta}$ films. In such hybrid polymer/superconductor systems, it is found that, when the polymer is oxidized to its conductive state, the transition temperature (T_c) and critical currents (J_c) of the underlying superconductor film are suppressed. Reversible modulations of the transition temperatures of up to 50 K are noted for these structures. Upon reduction of the conductive polymer layer back to its nonconductive form, both T_c and J_c are found to return to values close to those acquired for the underivatized $YBa_2Cu_3O_{7-\delta}$ film.

1. Introduction

In 1986, J. G. Bednorz and K. A. Müller discovered superconductivity at 35 K in $La_{1.85}Ba_{0.15}CuO_4$ and ushered in an era of renewed interest in the field of superconductivity.[1] Ensuing research was conducted at a furious pace, and new compounds with even higher transition temperatures were soon discovered. Within a year of the report by Bednorz and Müller, $YBa_2Cu_3O_7$ was discovered to have a transition temperature of over 90 K,[2] and for the first time, superconductivity could be observed while using a relatively inexpensive liquid nitrogen cryogen. By January of 1988, the BiSrCaCuO system was discovered to possess a record T_c of 105–120 K. Only one month later, the record held by the BiSrCaCuO system was surpassed by the discovery of the TlBaCaCuO system with a T_c of 125 K.[3–7]

Since this time, the pace in discovering new superconductors has slowed somewhat. However, the recent discovery of the $HgBa_2Ca_2Cu_3O_8$ (Hg-1223) system pushes record T_c values to over 133 K[8] at ambient pressure while a T_c as high as 153 K has been observed for Hg-1223 at 150 kbar.[9] One group has even reported an astounding T_c of 250 K for extremely thin films of BiSrCaCuO,[10] but this has yet to be confirmed by other researchers, and the search for cuprates with even higher transition temperatures continues.

Unfortunately, the poor physical properties exhibited by these reactive[11,12] and brittle ceramic compounds continue to inhibit the practical utilization of these superconductors. In an effort to overcome some of these problems, a number of research groups have initiated studies designed to explore conductive polymer systems in the context of high-T_c applications. Such polymers offer both the prospects for enhanced processability as well as a wide range of electrical conductivities. Conductive polymer systems can be doped reversibly from neutral, nonconductive forms (10^{-8}–10^{-5} Ω^{-1} cm^{-1}) to oxidized states which display high electrical conductivities (10^{1}–10^{5} Ω^{-1} cm^{-1}). In their nonconductive forms, the electronic interactions between conductive polymers and superconductors are expected to be minimal. Such materials may find utility in the context of providing environmental barriers to protect the superconductor against the adverse effects of corrosion. On the other hand, the doped polymer materials when placed in intimate contact with a superconductor can exchange their electrons (or holes) with those in the superconductor. Thus, the use of conductive polymers may provide an alternative strategy for the construction of superconductor devices[13,14] and circuits. Moreover, these hybrid assemblies can be utilized to study fundamentally interesting issues related to electron and energy transfer phenomena which occur at molecule/superconductor interfaces at temperatures above and below T_c.[14–16]

Although a variety of synthetic techniques can be utilized to prepare composite conductive polymer/superconductor systems,[17–19] electrochemical growth of polymers onto the surface of superconductors is by far the most common method. Important for the preparation of these structures is the elimination of the surface degradation of the high-T_c compounds. For example, the preparation of polyaniline films is normally accomplished using an acidic solvent. Although the use of such corrosive fluids is not problematic for the deposition of polyaniline films onto noble metal electrodes such as Pt or Au, growth of polyaniline

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onto $YBa_2Cu_3O_{7-\delta}$ has been reported to result in the loss of up to 20% of the superconductor.[19]

Maintaining pristine polymer/superconductor interfaces is essential for the formation of good electrical contact between the two conductors. In this regard, we have shown that carefully dried, nonaqueous solvent systems, such as acetonitrile and methylene chloride, can be utilized successfully for the clean electrodeposition of conductive polymer films onto $YBa_2Cu_3O_{7-\delta}$,[14] the most reactive cuprate material.[11] Moreover, maintaining the electrochemical potential window between −1.3 and +1.4 V vs SCE is necessary to avoid damage of the superconductor electrode template.[20]

In addition to the decomposition of the superconductor elements, many of the conductive polymer systems tend to degrade chemically and lose their conductive properties when exposed to the atmosphere.[21] On the other hand, polypyrrole is one of the most environmentally stable conductive polymers available when in its oxidized form. Pyrrole can be electrochemically polymerized at relatively low potentials which make it an ideal candidate for the fabrication of polymer/superconductor composite systems.

The focus of this paper will be placed on a discussion of the preparation, analysis, and properties of hybrid conductive polymer/superconductor structures. Atomic force microscopy (AFM), scanning electron microscopy (SEM), and electrochemical techniques are used to characterize polypyrrole growth onto $YBa_2Cu_3O_{7-\delta}$ thin film electrodes. Cyclic voltammetry and normal-state resistivity measurements are utilized to explore issues related to the compatibility of the conductive polymer and cuprate superconductor elements in these composite structures. Electrochemical techniques are also used to grow as well as to control the oxidation level of the polypyrrole layers that are localized on the surface of $YBa_2Cu_3O_{7-\delta}$ thin films. In addition, changes in the properties of the superconductor element in the bilayer structures are monitored as a function of polymer oxidation level.

2. Experimental Section

Acetonitrile (Burdick and Jackson) and pyrrole (Aldrich) were dried by passing the liquids over freshly activated alumina and then were stored over 3 Å molecular sieves. Tetraethylammonium tetrafluoroborate (Aldrich) was recrystallized three times from methanol/petroleum ether and dried for 36 h at 75 °C in vacuo.

A PAR 273 potentiostat, interfaced to an IBM PS/2 model 55 SX computer, was utilized to acquire the electrochemical data. Experiments were performed in the normal three-electrode mode. Potentials were measured with respect to a silver wire quasi-reference electrode and adjusted to SCE values using ferrocene as an internal redox standard. The majority of the electrochemical experiments were completed in an Innovative Technology MB 150 M (Newburyport, MA) inert atmosphere glovebox.

For the superconductor microbridge experiments, freshly deposited (unless otherwise noted) $YBa_2Cu_3O_{7-\delta}$ thin films were used as the working electrodes. Polymerization reactions were completed from solutions of 0.25 M Et_4NBF_4 in neat pyrrole for the preparation of the bilayer structures by using both voltammetric and potential step techniques. Using such methods, the potential of the superconductor electrode was raised to values in the range 0.7–1.0 V vs SCE. Apiezon wax was utilized to localize the polypyrrole growth to desired locations on the superconductor electrode template. The wax was then removed with dry toluene prior to the analysis of the composite structures.

In a similar fashion, polypyrrole films were deposited onto Pt and $YBa_2Cu_3O_{7-\delta}$ electrodes for AFM characterization using dilute pyrrole solutions. The majority of the experiments were completed with solutions of 50 mM Et_4NBF_4 in 0.14 M pyrrole/acetonitrile. Potential step excursions using an applied voltage of 1.25 V vs SCE for Pt and 1.35 V vs SCE for $YBa_2Cu_3O_{7-\delta}$ for 40 s in both cases were utilized to generate polypyrrole films of comparable thickness. In other experiments, films were deposited from 0.1 M Et_4NBF_4 in 0.14 M pyrrole/acetonitrile using a single voltammetric cycle from −0.27 to 1.2 V vs SCE at 50 mV/s as well as with the use of a potential step excursion to 1.2 V vs SCE for 2–10 s.

Electrochemical doping was performed using monomer-free solutions of 0.1 M Et_4NBF_4 in acetonitrile. Oxidative doping of the polymer into the conductive form was accomplished by raising the potential of the superconductor electrode to values of ~0.7 V vs SCE. The maximum room temperature conductivities of such doped polymer films were found to be ~50 Ω^{-1} cm^{-1} for polypyrrole, close to values reported previously.[21]

Thin films of $YBa_2Cu_3O_{7-\delta}$ (~200–5000 Å in thickness) were deposited onto single crystalline MgO (100) and $LaAlO_3$ (100) substrates using the pulsed laser ablation method.[22] After establishing a base vacuum of ~10^{-6} Torr, 150 mTorr of oxygen was introduced into the deposition chamber and the films were deposited with a substrate temperature of ~750 °C for *c*-axis films, 730 °C for *a*/*c*-axis films, and 700 °C for *a*-axis films. A KrF excimer laser operating at 248 nm was used to irradiate a ceramic target of $YBa_2Cu_3O_{7-\delta}$. Following the deposition, the thin film was cooled to ~450 °C and 1 Torr of oxygen gas was introduced for the annealing step which typically lasted about 15 min.

The films of $YBa_2Cu_3O_{7-\delta}$ were characterized by four-point probe conductivity, scanning electron microscopy, and X-ray powder diffraction measurements. To explore the polymer/superconductor interactions, microbridges (~3 mm long and ~100 μm wide) were created[23] on the $YBa_2Cu_3O_{7-\delta}$ film by scribing the superconductor layer with a diamond tip controlled by a micromanipulator or by using a laser etching technique. The laser patterning method employed a metal mask and a number of excimer laser pulses to ablate away the unwanted superconductor regions. In certain cases, films of $YBa_2Cu_3O_{7-\delta}$ were produced which exhibited poor morphologies as well as a large number of defects. Films of this type tended to be more sensitive to the influence of the conductive polymer layers. Better defined weak links were created by depositing the superconductor over the natural step edges that exist on the surfaces of cleaved and unpolished MgO (100) substrates. Critical current measurements were completed using $YBa_2Cu_3O_{7-\delta}$ films in which a microbridge was created. One voltage and one current lead were attached to either side of the microbridge using an evaporated gold contact layer and gold paste. Current–voltage curves were obtained and J_c values were determined using the 1 μV/cm criterion.

3. Results and Discussion

A. Polypyrrole Growth onto $YBa_2Cu_3O_{7-\delta}$. Before details related to the growth of conductive polymer materials onto high-T_c surfaces can be understood completely, it is useful to study growth of the polymers under similar conditions at noble metal electrodes. Previous voltammetric studies conducted using platinum as a working electrode[24,25] have shown that, on the initial sweep, pyrrole is oxidized at the electrode surface to form solution-dissolved radical-cation species which couple to form dimers. The resulting dimers can be oxidized at lower potentials and can combine with other radical ions to form oligomers. These oligomers continue to grow in length to form a polymeric layer which eventually coats the electrode surface. This behavior is clearly apparent in the voltammetry acquired at Pt for a neat pyrrole solution. In the initial scan, higher potentials are required to oxidize the pyrrole solution (Figure 1a). Subsequent cycles yield oxidative currents at lower potentials. Here, the electrochemical behavior is dominated by the more easily oxidized oligomers (Figure 1b). In addition, the initial sweeps on platinum display the characteristic "nucleation loop" [25] in which the current on the reverse sweep is greater than the current in the forward sweep, indicating that nucleation of polymeric structures onto the electrode surface has begun to occur. Subsequent cycles produce successively larger oxidation currents which point to bulk polymer growth on the electrode surface.

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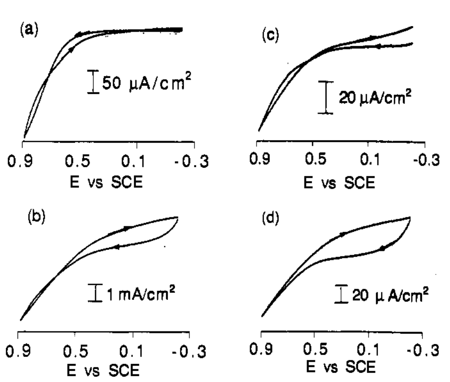

Figure 1. Cyclic voltammetry acquired for the growth of polypyrrole from a solution of 0.25 M Et_4NBF_4 in neat pyrrole for the following situations: (a) growth on a Pt film for the first scan, (b) growth on a Pt film for the 10th scan, (c) growth on a $YBa_2Cu_3O_{7-\delta}$ film for the first scan, (d) growth on a $YBa_2Cu_3O_{7-\delta}$ film for the 10th scan. All data were acquired using a scan rate of 100 mV/s.

Interestingly, the same general behavior is seen when a superconductor thin film is employed as the working electrode. In this regard, nucleation loops are observed for the initial scans (Figure 1c) and are lost in subsequent scans (Figure 1d) where bulk film growth is observed. The similarity of the voltammetry between that acquired at Pt electrodes and that obtained at $YBa_2Cu_3O_{7-\delta}$ electrodes demonstrates that electrical charge flows readily between polypyrrole and $YBa_2Cu_3O_{7-\delta}$ at room temperature and that the growth mechanisms are probably similar. However, careful analysis of the current densities for the polymer growth reveals that the growth rate is often much slower at the superconductor than that obtained at a platinum electrode.

The retarded growth observed for the superconductor surface is due, at least in part, to surface degradation of the cuprate film in certain regions. Unlike platinum electrodes that possess chemically robust surfaces, the superconductor interfaces are damaged readily upon exposure to the atmosphere. Parasitic corrosion reactions which occur when high-T_c materials are exposed to water, CO_2, CO, and acids have been shown to inhibit electron transfer reactions which occur at cuprate surfaces.[11,15,20,26] As a result, the actual electrochemically-active area of the high-T_c specimen may be considerably less than that of the geometric area, depending on the exposure history of the high-T_c electrode.

In previous electrochemical studies in which encapsulated pellets of the superconductor were used as the working electrodes, procedures were developed in which the surface of the electrode was polished periodically to remove the insulating degradation phases from the electrode surface. Such surface treatments were shown to dramatically improve the performance of the high-T_c electrodes.[26] Unfortunately, these treatments are not suitable for use with the thin films of $YBa_2Cu_3O_{7-\delta}$. However, an immersion of the $YBa_2Cu_3O_{7-\delta}$ film in a 1% solution of Br_2 in ethanol can be used to remove the surface degradation and restore a chemically pristine surface.[27] To explore this issue, chronoamperometry experiments were completed to follow the growth of polypyrrole onto segments of a superconductor film that had been stored in a desiccator for a period of 10 months. Prior to polymer deposition, the film was cleaved into two pieces. One half of the film was treated with a 7 min Br_2 etch prior to polymer deposition, and the other half was used without further treatment. The rate of polymer growth on the Br_2-etched electrode is much greater than that on the untreated film, as demonstrated by the three times greater amount of charge passed through it. The sluggish growth of polymer onto the untreated portion of the electrode is consistent with the accumulation of an insulating layer onto the surface of the cuprate film. Although the polymer grows eventually onto the degraded surface, the polymerization reactions likely are retarded by uncompensated resistance effects caused by the degradation layers as well as by the decrease in electroactive surface area. Etching by bromine yields a more active surface of the high-T_c film and appears to be an effective surface treatment procedure for the preparation of high-T_c thin film electrodes.

In order to explore further the deposition of conductive polymer layers onto high-T_c thin film electrodes, a series of AFM experiments were completed. Measurements of this type can provide nanometer resolution of the polypyrrole surface. To our knowledge, this is the first report of STM or AFM imaging of any conductive polymer system which is deposited onto a high-T_c template. Previously, STM/AFM methods have been used to image polypyrrole growth on highly oriented pyrolytic graphite (HOPG),[28] polyaniline on platinum,[29] polyaniline on gold,[30] poly(ethylene oxide) on HOPG,[31] and poly(1-aminoanthracene) on platinum.[32] Measurements of this type have shown that polypyrrole grows in strands during the initial stages of polymerization. These features expand in size as the growth continues and form a semicrystalline film composed of a series of micro islands.[28] Longer deposition times, however, result in an abrupt transition to an amorphous structure. These amorphous grains increase in diameter as the film thickens. Similarly, granular morphologies are observed for the other polymers.[21,22,24]

The physical structures and electrical properties of $YBa_2Cu_3O_{7-\delta}$ are highly anisotropic and are important issues that must be considered both in device fabrication using conventional solid-state materials and in making polymer/superconductor structures. To explore whether or not this anisotropy influences the growth of polypyrrole, a number of thin films were prepared having different crystallographic orientations. Figure 2 shows a series of $YBa_2Cu_3O_{7-\delta}$ films that possess *c*-axis, *a*/*c*-axis, and *a*-axis orientations. From the physical appearance of the films, it is clear that the *c*-axis films are much smoother than their a-axis counterparts. Films with mixed *a*/*c*-axis orientations exhibit intermediate behavior.

Images acquired by AFM for the initial stages of polypyrrole growth on Pt film electrodes show that the polymer nucleation occurs rapidly and evenly over the entire exposed surface (Figure 3a). Moreover, chronoamperometry and profilometry measurements indicate that the polymer growth is rapid on the noble metal electrodes. On the other hand, the smooth *c*-axis $YBa_2Cu_3O_{7-\delta}$ film supports only sporadic growth as polymer features are distributed only at remote sites on the surface of the film, as shown in Figure 3c. Accordingly, chronoamperometry measurements support the notion that polymer growth is retarded on the *c*-axis-oriented film. Interestingly, the rougher *a*/*c*-axis mixed $YBa_2Cu_3O_{7-\delta}$ thin film electrode fosters more rapid and uniform growth of the polymer, as shown in Figure 3b. Here polypyrrole forms a uniform coating over the entire exposed surface. Comparison of the different orientations of the $YBa_2Cu_3O_{7-\delta}$ films show clearly that more favorable electrochemical behavior is obtained at the *a*-axis grains. Moreover, this data forms the basis for a new method that can be used to evaluate the local surface conductivity properties of high-T_c structures. This electrochemical decoration method may find utility in the area of high-T_c device process development.

B. Electrochemical Doping of Polypyrrole. In addition to providing reliable procedures for depositing polypyrrole layers

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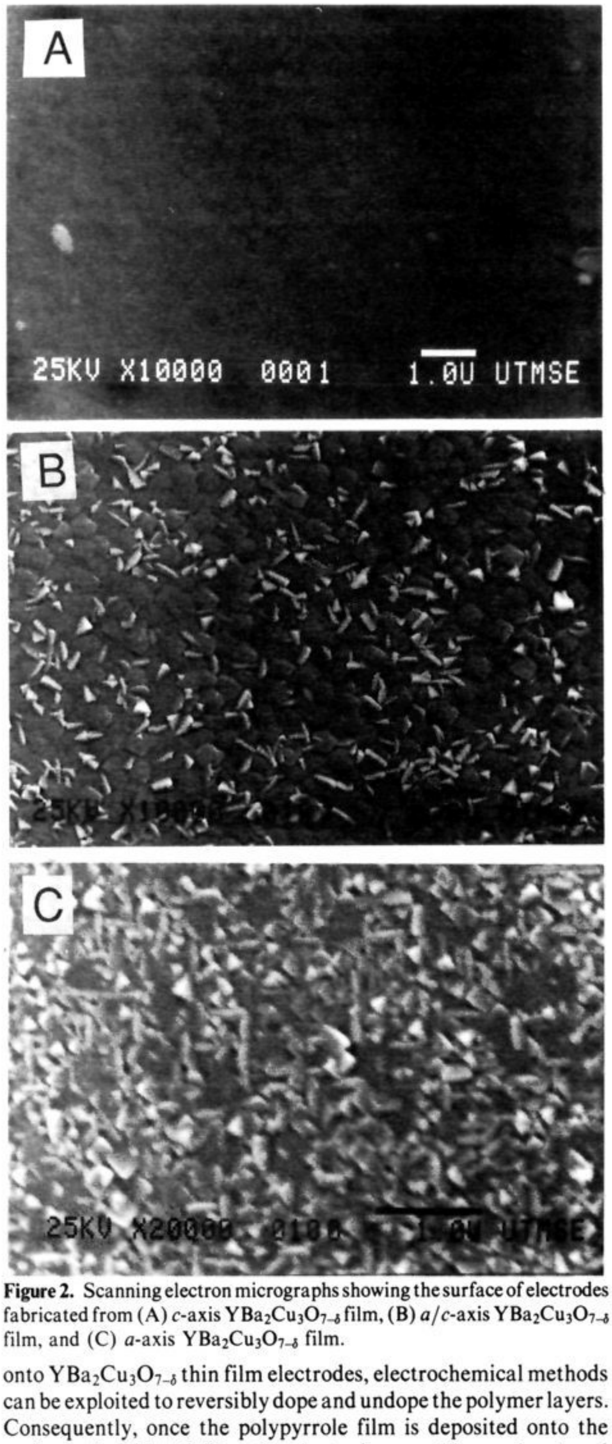

Figure 2. Scanning electron micrographs showing the surface of electrodes fabricated from (A) *c*-axis $YBa_2Cu_3O_{7-\delta}$ film, (B) *a*/*c*-axis $YBa_2Cu_3O_{7-\delta}$ film, and (C) *a*-axis $YBa_2Cu_3O_{7-\delta}$ film.

onto $YBa_2Cu_3O_{7-\delta}$ thin film electrodes, electrochemical methods can be exploited to reversibly dope and undope the polymer layers. Consequently, once the polypyrrole film is deposited onto the surface of a high-T_c film, the electrode assembly can be placed in a monomer-free electrolytic solution and the polymer can then be reversibly cycled between its neutral and oxidized forms. Figure 4 displays doping and undoping cycles for a film of polypyrrole on the superconductor as studied by chronoamperometry. The close agreement between the magnitudes of the oxidative and reductive currents demonstrates that the passage of current between the high-T_c and polymer components occurs quite readily, as is the case for noble metal electrodes.[33] Aside from the initial sluggish growth on the superconductor, both chronoamperometry and cyclic voltammetry measurements show that the polymer displays almost identical behavior on Pt electrodes as on $YBa_2Cu_3O_{7-\delta}$ thin films.

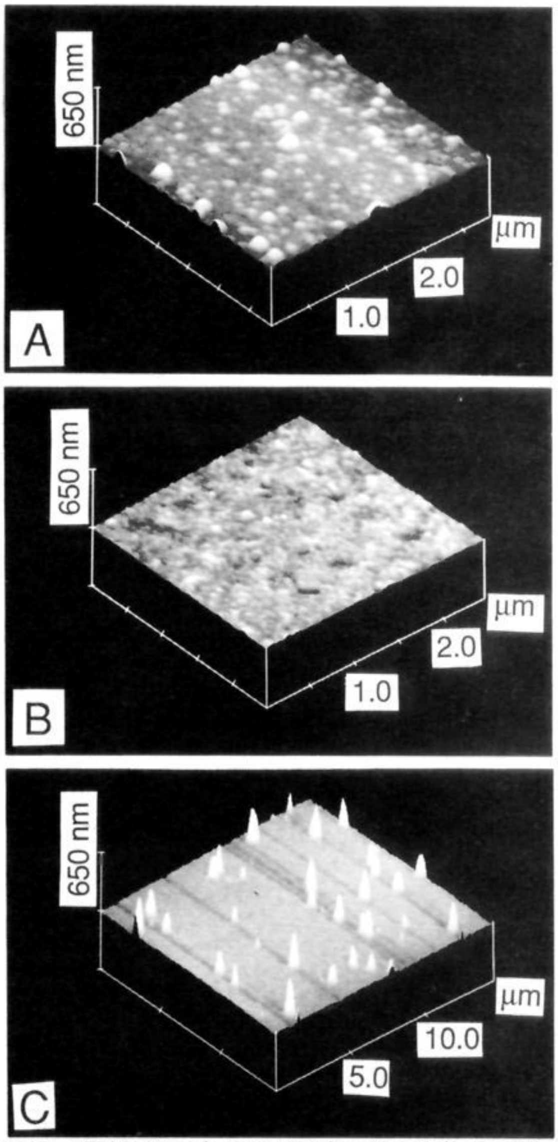

Figure 3. AFM images of polypyrrole electrodeposited onto (A) a Pt film by potential step to 1.2 V vs SCE for 5 s, (B) *a*/*c*-axis $YBa_2Cu_3O_{7-\delta}$ film by potential step to 1.2 V vs SCE for 5 s, (C) *c*-axis $YBa_2Cu_3O_{7-\delta}$ film by potential step to 1.2 V vs SCE for 5 s. Polypyrrole films were formed from a 0.1 M Et_4NBF_4 in 1% (by volume) pyrrole/acetonitrile solution.

C. Modulation of Superconductivity. One of the most important and interesting features associated with the conductive polymer/high-T_c superconductor structures involves the study of the polymer/superconductor electronic interactions which occur at temperatures below T_c. In order to facilitate such measurements, a procedure for preparing polymer-coated superconductor microbridge devices was developed[14] as illustrated in Figure 5. According to this method, $YBa_2Cu_3O_{7-\delta}$ is deposited onto a clean MgO(100) or $LaAlO_3$ (100) substrate using the laser ablation method. Film thickness values between 200 and 5000 Å are obtained by varying the number of deposition pulses. After characterizing the films by conductivity and X-ray powder diffraction methods, a microbridge is created in the central portion of the film using either laser etching or mechanical scribing procedures. In the final step, the polymer is deposited over the bridge using techniques similar to those described above. Figure 6 displays an image obtain by SEM of a typical polymer/superconductor bilayer microbridge.

The influence of the polymer doping level on the properties of the underlying superconductor were then examined. Although minor increases in the room temperature bridge resistance values

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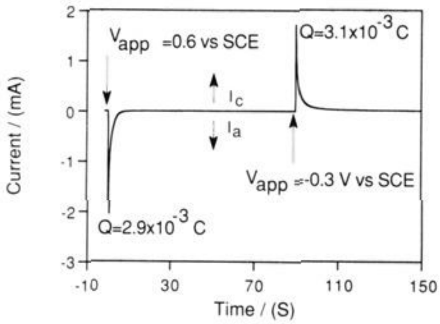

Figure 4. Current vs time traces acquired for a ~1000 Å thick film of polypyrrole coated onto a $YBa_2Cu_3O_{7-\delta}$ thin film electrode. Prior to the experiment, the polymer is reduced completely to its neutral form. The polymer layer is then oxidized to its conductive form by stepping the potential to 0.6 V vs SCE. After the current is decayed to the baseline value, the oxidized film is cycled back to the neutral form by applying a voltage of –0.3 V vs SCE. The experiment is completed in a solution of 0.1 M Et_4NBF_4/acetonitrile.

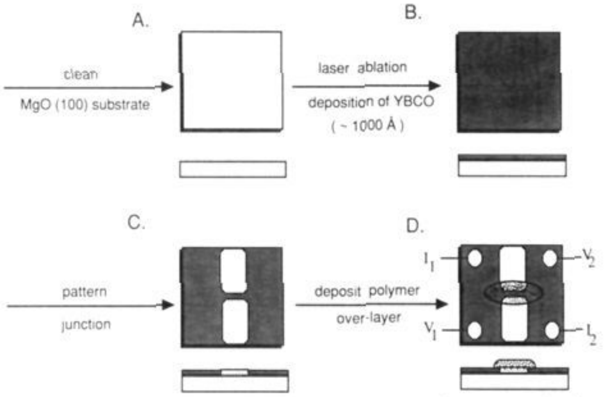

Figure 5. Schematic illustration showing the steps that are required to prepare the conductive polymer/high-temperature superconductor bilayer structures. First, a $YBa_2Cu_3O_{7-\delta}$ thin film is deposited onto a MgO (100) or $LaAlO_3$ (100) substrate using the laser ablation method. Next, a microbridge is patterned into the central portion of the film. Finally, a conductive polymer layer is deposited electrochemically onto the microbridge area.

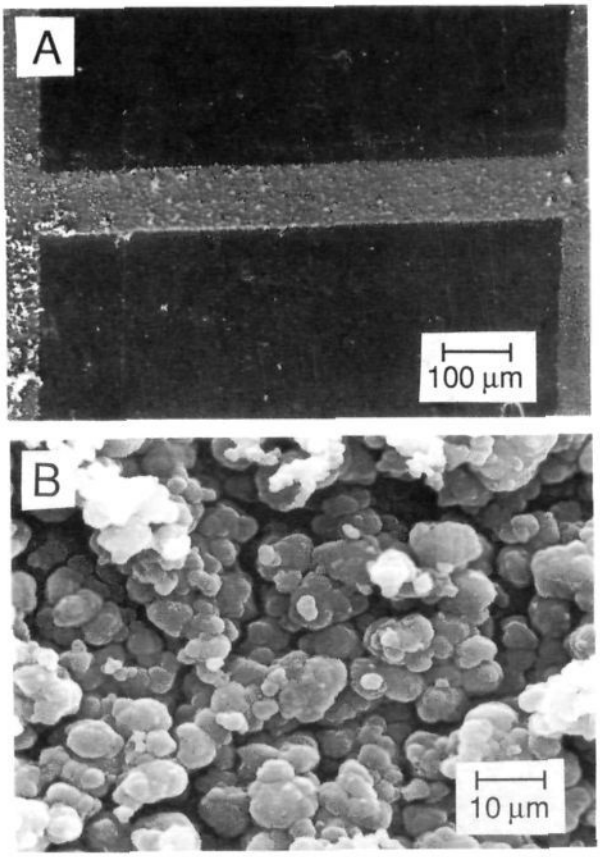

Figure 6. Scanning electron micrographs showing a 100 μm wide × 1.1 mm long $YBa_2Cu_3O_{7-\delta}$ microbridge that has been coated with a ~3 μm thick film of polypyrrole. The bridge was created with a laser etching method in which two pulses of an excimer laser were utilized to ablate away the regions adjacent to the bridge: (**A**) a low-magnification view shows the entire bridge and (**B**) a higher magnification shows the center portion of the bridge which is coated with nodules of polypyrrole.

were noted after polymer deposition, the most dramatic changes were observed for the superconducting properties. Figure 7 displays a series of resistance vs temperature curves for $YBa_2Cu_3O_{7-\delta}$ microbridges of variable superconductor thicknesses coated in each case with ~2 μm of polypyrrole. When a 1200 Å thick film of $YBa_2Cu_3O_{7-\delta}$ is employed (not shown), very little changes in the properties of the superconductor are noted as the polymer is cycled between its neutral and oxidized forms. In both cases, the transition temperatures for the polymer-coated films are very close to those obtained for the uncoated structure. For the thinnest superconductor element (Figure 7a) composed of a ~200 Å film of $YBa_2Cu_3O_{7-\delta}$, superconductivity with an onset temperature close to 75 K is noted for the uncoated bridge. On the other hand, the same microbridge when coated with the polymer in its oxidized form displays no signs of superconductivity down to 22 K, the lowest temperature measured. Although it is relatively easy to suppress superconductivity permanently (i.e., through corrosive damage of the material), it is challenging to develop methods that can be used to reversibly modulate superconductivity. However, after the room temperature reduction of the polymer, the transition temperature of the bridge is found to return to a value very close to that of the bare bridge. This greater than 50 K modulation of superconductivity is, to our knowledge, the largest reversible shift in superconductivity reported to date. The superconductor film with the intermediate thickness value (Figure 7b) displays a reversible shift ofsuperconductivity on the order of 14 K. In each case, a weakening of superconductivity is noted from a lowering of the transition temperature when the polymer is oxidized. Moreover, cycling of the polymer between its oxidized (conductive) and neutral (insulating) forms can be accomplished several times, yielding similar behavior (provided that the electrochemical potentials are not taken to extreme values and corrosive reagents such as water are not present in the electrolytic fluid). When precautions are taken to avoid chemical damage of the superconductor, modulation of T_c is reproducible. In addition to modulation of T_c, it is also noted that the critical current values, J_c, are affected by the oxidation state of the conductive polymer layer. Figure 8 displays the current–voltage traces for a single bridge covered with polymer examined both for the neutral and oxidized forms of the polymer. Evident here is the fact that the critical current is suppressed by the presence of the doped polymer and increases after the room temperature reduction of the polymer to its neutral form.

Immediately apparent from the data is the fact that the magnitude of the modulation of superconductivity is tied closely to both the polymer oxidation level as well as the superconductor film thickness. Films with thickness values greater than ~1000 Å display virtually no modulation of superconductivity, whereas very thin films exhibit the largest changes in T_c.

The magnitude of the modulation of the superconducting properties in the conductive polymer/high-T_c superconductor bilayer structures is also dependent upon the superconductor film morphology. Films with thickness values greater than 1000 Å, regardless of the film morphology, normally display little to no measureable shift in T_c. Thin films of the superconductor with

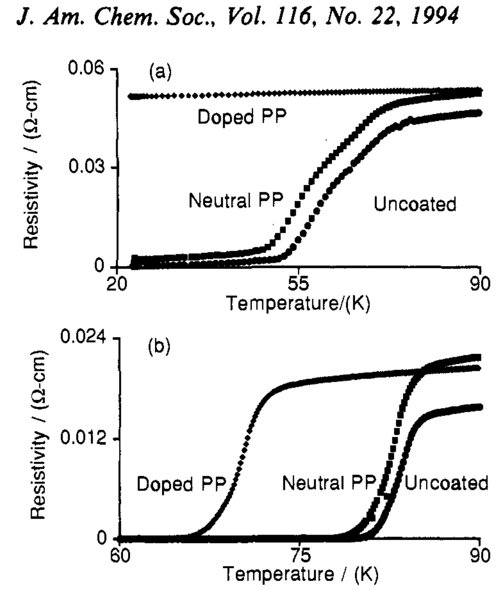

Figure 7. Resistance vs temperature curves acquired for ~100 μm wide × 3 mm long microbridges formed from $YBa_2Cu_3O_{7-\delta}$ films. Data are provided here for superconductor films of variable thicknesses: (a) ~200 Å $YBa_2Cu_3O_{7-\delta}$ on MgO step edges (film thickness reported here refers to the value in the step edge region and is estimated from SEM pictures as well as from critical current values and (b) ~500 Å $YBa_2Cu_3O_{7-\delta}$ on polished MgO (100). Initial data were acquired for the bare bridges, then bridges were coated with ~2 μm of doped polypyrrole, and finally the polymer overlayers were reduced to the undoped form.

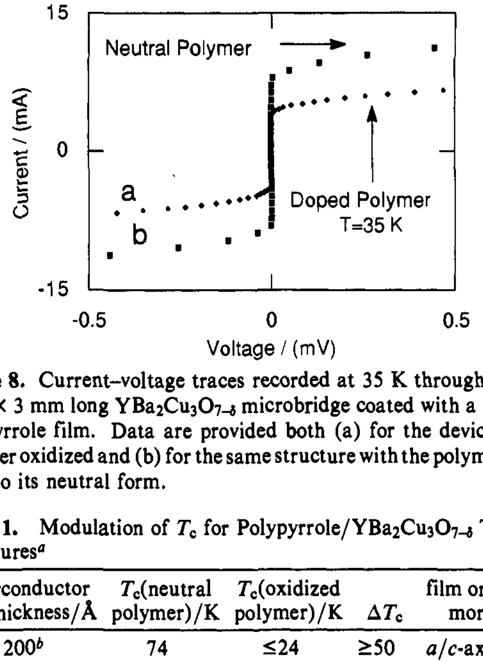

Figure 8. Current–voltage traces recorded at 35 K through a 100 μm wide × 3 mm long $YBa_2Cu_3O_{7-\delta}$ microbridge coated with a 2 μm thick polypyrrole film. Data are provided both (a) for the device with the polymer oxidized and (b) for the same structure with the polymer reduced back to its neutral form.

Table 1. Modulation of T_c for Polypyrrole/$YBa_2Cu_3O_{7-\delta}$ Thin Film Structures[a]

superconductor film thickness/Å	T_c(neutral polymer)/K	T_c(oxidized polymer)/K	ΔT_c	film orientation/ morphology
200[b]	74	≤24	≥50	a/c-axis/rough
500	84	70	14	a/c-axis/rough
1500	80	79	1	a/c-axis/rough
500	87.6	86.8	0.8	c-axis/smooth
900	87.6	87.0	0.6	c-axis/smooth
1200	87.0	87.0	0	c-axis/smooth

[a] Each superconductor device was coated with 2 μm polypyrrole film. [b] Reported thickness represents the estimated superconductor thickness over the step for a 800 Å film of $YBa_2Cu_3O_{7-\delta}$ that was deposited over a 1500 Å step edge.

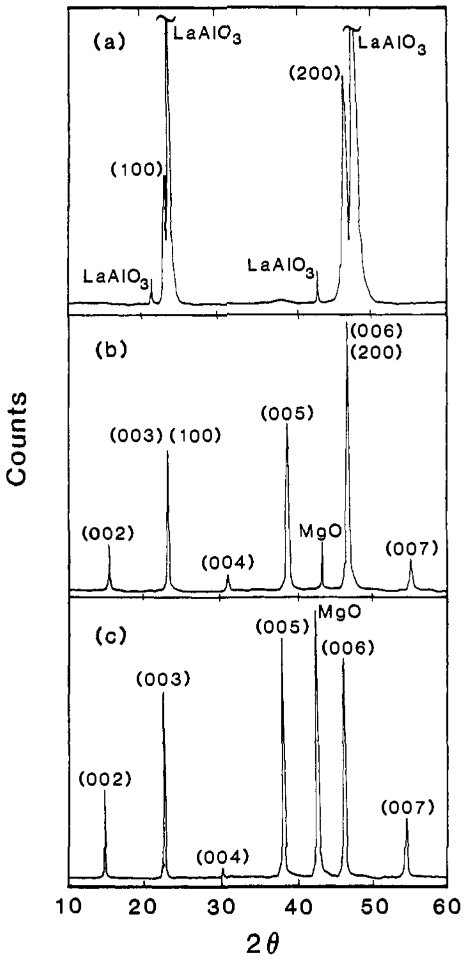

Figure 9. X-ray powder diffraction patterns for the following samples: (a) a-axis $YBa_2Cu_3O_{7-\delta}$ thin film on $LaAlO_3$ (100), (b) $YBa_2Cu_3O_{7-\delta}$ thin film with a mixed a/c-axis orientation on MgO (100), and (c) $YBa_2Cu_3O_{7-\delta}$ thin film c-axis orientation on MgO (100).

rough morphologies and high a-axis content show the greatest change in T_c, whereas the smooth films are influenced by the polymer only to a minor extent. Summarized in Table 1 are transition temperatures for the polymer/superconductor devices in both the neutral and oxidized forms for various thickness values and morphologies of the superconductor thin films. The first three sets of data are for cases where highly textured films of mixed a/c-axis were used, and the latter three sets correspond to data acquired for smooth c-axis films.

There are a number of important differences between the rough and smooth films that may be responsible for the differences in the magnitude of the modulation of superconductivity. First, rough films possess regions which are much thinner than the average value. Locally, these weak link structures possess critical current values that are much less than that of the remainder of the film and contribute to the enhanced sensitivity of such regions. Second, the polycrystalline films possess both a-axis and c-axis crystallographic orientations (vide infra). Since the coherence length along the c-axis (ξ_c ~ 1.5–4 Å) is much shorter than that along the a-axis (ξ_{ab} ~ 20–50 Å), the inclusion of an a-axis component into the device may serve to increase the sensitivity of the hybrid structure. Finally, the textured films possess polycrystalline film orientations which result in a large number of high-angle grain boundaries that are highly sensitive to external stimuli.

Although deposition conditions for the preparation of $YBa_2Cu_3O_{7-\delta}$ films are often tailored to produce c-axis-oriented films which exhibit high critical currents, polycrystalline films appear to be better suited for the fabrication of conductive polymer/superconductor structures. Figure 9 presents X-ray powder diffraction data obtained for (a) an a-axis film on $LaAlO_3$ (100), (b) a polycrystalline film of $YBa_2Cu_3O_{7-\delta}$ on MgO (100) prepared with the low-density target, and (c) a c-axis film on MgO (100). Although, the two films deposited using the high-density target exhibit almost exclusively c-axis and a-axis orientations, respectfully, the film fashioned with the low-density target possesses mixed c- and a-axis orientations.

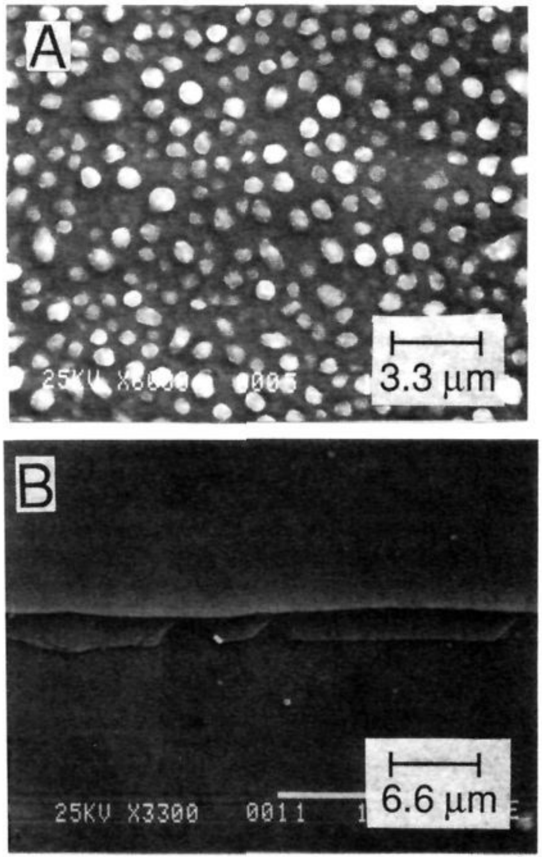

Figure 10. (A) Scanning electron micrograph showing a ~800 Å thick film of $YBa_2Cu_3O_{7-\delta}$ that was deposited via laser ablation onto a cleaved MgO (100) substrate. Here, weakly coupled grains of superconductor regions form poor electrical contact to neighboring grains. (B) Scanning electron micrograph showing a film of $YBa_2Cu_3O_{7-\delta}$ that was deposited via laser ablation onto a cleaved MgO (100) substrate. Weakly coupled superconductor regions are formed at the step edges which exist on cleaved but unpolished substrates.

Low-density targets appear to be effective for the deposition of rough high-T_c thin films. Such targets are not uniformly ablated on the atomic level, but rather these targets produce plumes of ablated material that consist of small particles of the superconductor. The resulting superconductor thin films are more textured and have lower critical currents than the smooth films formed from high-density targets. Figure 10a shows an image of a $YBa_2Cu_3O_{7-\delta}$ film created by laser ablation from a low-density target. The weak link characteristics of these thin films are also enhanced by depositing the superconductor onto a cleaved MgO substrate. These substrates possess natural step edges which can be exploited to further disrupt the connection between selected superconductor grains, as illustrated in Figure 10b. This specimen was utilized to create the superconductor/conductive polymer bilayer structure that displays the 50 K shift in T_c. The large grain size and rough texture of the superconductor element are readily apparent from the micrograph.

Similarly, Mannhart[34] et al. have prepared films rich with weak links for the purpose of making electric field effect devices which exhibit high sensitivities. To prepare such devices, the substrates were polished with 1 μm diamond paste prior to superconductor deposition. The diamond polishing procedure leads to the formation of a network of fine grooves on the substrate and induces the creation of grain boundaries in the film. Electric field devices fabricated from these weak link rich films have displayed large shifts in T_c (on the order of 10 K).

There are several possible explanations for the observed modulation of superconducting properties in these bilayer structures. Since $YBa_2Cu_3O_{7-\delta}$ reacts readily with water, CO, CO_2, and acids,[26,35,36] chemical degradation processes could account for the initial decrease in T_c. However, the subsequent restoration of superconductivity to higher temperatures is not at all consistent with such behavior. Furthermore, uncoated superconductor films were cycled electrochemically without polymer-modifying layers in control studies and no evidence was found for reversible modulation of T_c. These measurements were completed to determine whether or not the electrochemical treatment may be responsible for a reduction in the oxygen content of the underlying superconductor. Changes in the copper valence values which result from alterations in the oxygen content in $YBa_2Cu_3O_{7-\delta}$ have been shown previously to alter T_c. However, oxygen content changes are known to result in large changes in normal-state properties,[37] such as room temperature resistivity and the temperature dependence of the resistivity, and this is not observed. Thus, changes in the bulk oxygen content do not appear to be responsible for the observed behavior. However, the reversible changes in the chemical structure (i.e., oxygen content) may be limited to the grain boundaries and this might affect the superconducting properties of the film without causing major changes in the normal-state properties.

If the observed effects are not the result of chemical degradation or changes in the oxygen content, it is plausible that strong polymer/superconductor electronic interactions could occur in these hybrid systems. In this regard, two possible interactions must be considered. First, if the polymer layer is separated from the superconductor by an insulating barrier formed by superconductor degradation products, the observed modulation of superconducting properties may be the result of an electric field effect.[38-40] The applied field caused by the oxidized polymer may thereby influence the number of mobile charge carriers in the superconductor in a way that is analogous to the field effect in conventional metal oxide-semiconducting devices. Electric field effects for the modulation of superconductivity have been observed previously. While changes in T_c due to field effects are normally much less than those we have observed, recent studies have shown that the shift can be magnified by using films with weak link characteristics.[34] In our structures, we have found also that the greatest observed shifts are obtained when weak links are introduced into the superconductor component.

A second possibility is that a superconducting proximity effect[41,42] operates within the composite assembly. According to such an explanation, when normal metals and superconductors are brought into intimate contact with each other, a leakage of the Cooper pairs from the superconductor into the normal metal can occur along with quasiparticle (i.e., isolated electron) penetration from the metal into the superconductor. This phenomenon is most pronounced directly at the interface between the two conductors. For sufficiently thin metal films atop thick superconductor samples, a normally non-superconducting metal can be driven completely into the superconducting state by virtue of the effect. Conversely, thin superconductor specimens have been shown to revert back to a normal metallic state when they are placed on top of thick metal samples. In these studies, the doped conductive polymer layer may be acting as the normal

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metal layer in this regard. The large dependence upon superconductor thickness and the contact resistance data previously collected are consistent with this mechanism.[43]

The magnitude of the proximity effect observed for classical studies of metal/superconductor sandwich structures has been shown to be dependent on a number of factors such as the metal and superconductor thickness as well as the coherence length of the superconductor template.[44,45] The large shifts in T_c we have observed are inordinately large based on the very small coherence length ($\xi \sim 20$ Å) of $YBa_2Cu_3O_{7-\delta}$ and the relatively large average thickness values for the superconductor. However, these large shifts in T_c are only observed with films that have a large number of weak links. We speculate that the presence of these weak links is a key factor in producing the large shifts in T_c that we have observed.

4. Conclusion

We have shown that polypyrrole can be grown electrochemically on very thin $YBa_2Cu_3O_{7-\delta}$ electrodes. The growth of the polymer is a function of both the surface quality and axis orientation of the electrode. In addition, the superconducting properties of the underlying $YBa_2Cu_3O_{7-\delta}$ film can be controlled by the oxidation state of the polymer. While the exact mechanism for the suppression of T_c has yet to be determined definitively, we have shown that the conductive polymer layers can be used to modulate reversibly the transition temperature of a superconductor microbridge by as much as 50 K. Moreover, the degree of modulation is highly dependent on the superconductor thickness as well as the presence of weak links within the sample.

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